

AD735161

A THEORETICAL STUDY OF SEPTET AND QUINQUET ELECTRONIC STATES
OF FeO WITH SINGLE IONIC STRUCTURE

A Special Technical Report
for

CALCULATION OF PHYSICAL PROPERTIES OF DIATOMIC MOLECULES

Principal Investigator: Dr. P. S. Bagus

International Business Machines Corporation
Monterey and Cottle Roads
San Jose, California 95114
(408) 227-7100 extension 7663

AFPA Order Number AFPA 1482

Program Code Number 9h20

Contract No. DAMC9-1 69 C 0080

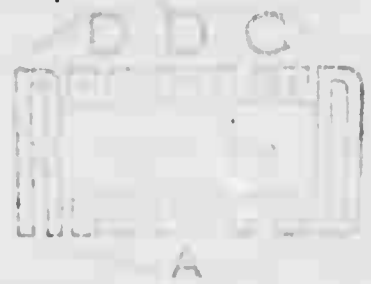
Effective Date: 18 June 1969

Expiration Date: 17 June 1972

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield Va 22151

DISTRIBUTION STATEMENT:

Approved for public release; distribution unlimited.



**BEST
AVAILABLE COPY**

A THEORETICAL STUDY OF SEPTET AND QUINTET ELECTRONIC STATES OF FeO WITH
SINGLY IONIC STRUCTURE

by

P. S. Bagus*

IBM Research Laboratory
San Jose, California

*This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by U.S. Army Research Office - Durham, Box CM, Duke Station, Durham, North Carolina 27706 under Contract No. DAHCO4-69C-0080.

ABSTRACT: Several states of septet and quintet spin of FeO are studied. Bound excited states of $7\Sigma^+$, $7\Sigma^-$, 7π , and $5\Sigma^+$ symmetry with $R_e \sim 3.7$ Bohrs and $D_e \sim 1.3$ eV are found. It is concluded that the ground state of FeO is not a septet state. It is possible that a quintet state with molecular structure similar to that of the states studied may be identified with the c state of FeO.

DISTRIBUTION STATEMENT:

Approved for public release; distribution unlimited.

I. INTRODUCTION

In the course of a series of Hartree-Fock calculations on FeO, a state of ${}^7\Sigma^+$ symmetry with an unusual molecular structure was obtained. The molecular orbital (MO) configuration of this state is - besides filled shells for the atomic cores - $7\sigma^2 8\sigma^2 9\sigma^1 10\sigma^1 3\pi^3 4\pi^3 1\delta^2$. The unusual aspect of this state is the fact that the molecular orbitals are almost entirely non-bonding. The last occupied σ orbital, 10σ , is primarily an Fe 4s orbital with a modest amount of 4p hybridization. The 4s-4p hybrid is directed out of the bond (away from O). From examinations of the MO's, particularly population analyses¹, the molecular structure is seen to strongly resemble that of an Fe^+ ion plus an O^- ion. The configuration of the Fe^+ ion is $3d^6(5D) 4s^1 4p^2$; in terms of orbitals with molecular symmetry it is

$$3d\sigma^1 3d\pi^3 ({}^2\Pi) 3d\delta^2 ({}^3\Sigma^-) 4s^1 4p\sigma^2$$

The configuration of O^- is $2p\sigma^2 2p\pi^3$.

The choice of the STO basis set for the analytic open shell SCF^{2,3} calculations is discussed in Sec. II and the results of the SCF calculations on the ${}^7\Sigma^+$ state are presented in Sec. III. The computed equilibrium separation is 3.73 Bohrs. The dissociation energy computed with respect to the restricted Hartree-Fock energies of the neutral ground state atoms is 1.3 eV.

A large number of molecular wave functions can be constructed from the model of Fe^+ and O^- described above. This is done by distributing the Fe^+ d and O^- p electrons in different ways among the nearly degenerate $d\sigma$, $d\pi$, and $d\delta$ and $p\sigma$ and $p\pi$ MO's and by coupling the angular momenta of the open shells in different ways. Some of the states which could be

constructed in this way were investigated and four potential curves almost parallel to and very near the ${}^7\Sigma^+$ state curve were found. These states were investigated by means of very limited CI calculations. The results of these calculations were equivalent to frozen orbital calculations. In this context, frozen orbital calculations mean calculations in which the SCF MO's of the ${}^7\Sigma^+$ state are used to construct one configuration wave functions for other states. The results of these calculations are presented in Sec. IV.

Some simple arguments are given in Sec. V to show that the molecular correlation energy of the states considered is very close to the correlation energies of the separated atoms. It is concluded, in Sec. VI, that the curves obtained are for fairly highly excited states of FeO. It is also concluded that the ground state of FeO is not a septet state.

II. SLATER TYPE BASIS SET

A reasonably large Slater Type (STO) basis set based on carefully optimized atomic basis sets was used for the calculations reported in this paper. As is well known³, an STO basis function, χ , is defined by:

$$\chi = N r_a^{n-1} \exp(-\zeta r_a) y_{\ell m}(\theta_a, \phi_a); \quad (1)$$

where N is a normalization factor, n is referred to as the principal quantum number, ζ is referred to as the basis function exponent, and the coordinates r_a , θ_a , and ϕ_a are measured with respect to center a . The atomic SCF calculations to be discussed below were all obtained using an open-shell restricted Hartree-Fock^{2,3,4} formalism. In this context, restricted Hartree-Fock means that all the orbitals in a shell are constrained to have the same radial parts.

The starting point for the basis functions centered on Fe was an 8s, 5p, and 4d STO basis set optimized for the $5D$ state of Fe by Bagus and Gilbert⁵. This basis set yields a restricted Hartree-Fock^{2,3} energy of -1262.4427 a.u. for the $5D$ state of Fe. (Clementi⁶ using a basis set of 11s, 6p, and 5d STO's obtained -1262.4425 a.u. and the energy obtained from numerical integration of the Hartree-Fock integro-differential equations^{4,7} is -1262.444 a.u.) This atomic basis set for Fe was supplemented with 2 4p and 2 4f STO's for the molecular FeO calculations. The two 4p exponents were chosen to be approximately 10% smaller than the 4s exponents in the atomic Fe basis set. These exponents were added to allow for polarization of the 4s shell of Fe. The two 4f exponents were chosen to span roughly the same space as the three smaller 3d STO's. These additional exponents were not optimized.

The starting point for the basis functions centered on O was a 5s and 5p STO basis set optimized for O^- by Clementi⁶. This basis yields an SCF energy of -74.78948 a.u. for $O^-(2p)$. We have also calculated an SCF wave function neutral O with the same basis set and obtain an energy of -74.8065 a.u. for O (3p); this should be compared with the energy of -74.80938 a.u. for O (3p) obtained by Bagus and Gilbert⁵ by optimizing the basis set for neutral O. The numerical Hartree-Fock^{4,7} energies for O (3p) and $O^-(2p)$ are, respectively, -74.80941 a.u. and -74.7897 a.u. Thus this O basis set is quite satisfactory for calculations on atomic O and O^- . This basis set was supplemented with 3 3d' STO's for the molecular FeO calculations. The 3d exponents are the same as have been used in several recent calculations⁸ on other metal monoxides (LiO, AlO, MgO and TiO) and CO, NO, and O₂.

The basis set for the molecular FeO calculations was formed from the one center STO's on Fe and O, described above, by constructing all possible basis functions of σ , π , and δ symmetries. The details of the basis set are given in Table I. From previous experience with diatomic molecular SCF calculations⁹, it is reasonable to estimate that the SCF energies obtained for FeO using this basis set will be within .01 a.u. of the Hartree-Fock limit.

III. SCF RESULTS FOR THE $^7\Sigma^+$ STATE OF FeO

The SCF calculations reported here were performed using the ALCHEM quantum chemistry program system¹⁰. The open shell SCF formalism used is an extension of Roothaan's analytic open shell SCF formalism³ to systems with more than one open shell per symmetry. As with Roothaan's earlier formalism³, the matrix SCF equations, including the off-diagonal Lagrange multipliers, are solved without approximation.

The electronic configuration of the $^7\Sigma^+$ state is:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^1 10\sigma^1 1\pi^4 2\pi^4 3\pi^3 4\pi^3 1\delta^2.$$

The 1σ through 6σ and 1π and 2π MO's represent the atomic cores; i.e., the $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals of Fe and the $1s$ orbital of O. No further reference will be made to these orbitals. The coupling of the remaining shells is as follows:

$$\left\{ 7\sigma^2 8\sigma^2 \left[9\sigma(^2\Sigma^+) 10\sigma(^2\Sigma^+); ^3\Sigma^+ \right] \left[3\pi^3(^2\pi) 4\pi^3(^2\pi); ^3\Sigma^- \right] 1\delta^2(^3\Sigma^-) \right\}; ^7\Sigma^+.$$

The SCF wave function for the configuration described above is invariant under a unitary transformation of the 9σ and 10σ orbitals. A unique choice of these orbitals was made by setting the off-diagonal Lagrange

multiplicities $\epsilon_{9\sigma,10\sigma} = \epsilon_{10\sigma,9\sigma} = 0$. This is equivalent to the usual choice of canonical SCF orbitals for closed shells¹¹.

SCF calculations have been performed at 6 internuclear separations: $R = 3.2$ (.2) 4.2 ; the computed potential curve is given in Figure 1. In Table II, we give population analyses¹, expectation values of z with respect to Fe and O, and orbital energies for the 7σ through 10σ , 3π , 4π , and 1δ orbitals for each computed internuclear separation. We also give total energies, values of V/T , dipole moments, and the gross atomic populations. The z -axis is the internuclear axis and is directed from Fe to O.

The calculated dissociation energy and equilibrium separation for the ${}^7\Sigma^+$ state are $D_e = 1.2$ eV and $R_e = 3.73$ a.u. The dissociation energy is computed with respect to the restricted Hartree-Fock energies of the neutral ground state Fe and O atoms. These energies⁵ are $E[O({}^3P)] = 74.8094$ a.u. and $E[Fe({}^5D)] = -1262.4427$ a.u. The minimum of the SCF potential curve for FeO was determined by making a quadratic fit to the calculated energies for $R = 3.6, 3.8$, and 4.0 a.u. A Dunham analysis¹¹ of the potential curve gave $\omega_e = 589$ cm^{-1} and $\omega_e x_e = 3$ cm^{-1} for ${}^{16}\text{O}$ and ${}^{56}\text{Fe}$.

Although there are small variations along the curve, the features of the MO's are very much the same for all the values of R considered. From the population analyses and expectation values of z given in Table II, we draw the following conclusions. The 7σ orbital is almost entirely O $2s$ with a small mixing of basis functions on Fe. The 8σ orbital is $\sim 90\%$ O $2p\sigma$ with $\sim 10\%$ of the charge on Fe; the charge on Fe decreases as the internuclear separation decreases. The 9σ orbital is almost entirely $3d\sigma$ on Fe. The 10σ orbital is $\sim 80\%$ Fe $4s$ and $\sim 20\%$ Fe $4p\sigma$; the negative value of $\langle z \rangle$ with respect to Fe shows that the sp hybridization is such that the charge is directed

away from the bond. The 3π , 4π and 1δ orbitals are non-bonding atomic orbitals which are respectively $3d\pi$ on Fe, $2p\pi$ on O and $3d\delta$ on Fe.

In summary, the charge distribution is nearly that of Fe^+ and O^- ; where for Fe^+ the valence shell structure (including the $3d$ shell) is $3d\sigma^1 3d\pi^3 3d\delta^2 4s^0 4p\sigma^2$ (^6H) and for O^- , it is $2p\sigma^2 2p\pi^3$ (^2H). The d -shell electrons of Fe^+ are coupled to ^5D which is by Hund's rule the energetically most favorable coupling. We note also that the wave function has the flexibility to dissociate to the ground states of the separated Fe and O atoms.

Decks of cards summarizing the SCF results, and including, in particular, the expansion co-efficients for the MO's, have been prepared. There are 158 cards for each internuclear separation. Copies of these decks are available upon request from the author.

IV. FROZEN ORBITAL RESULTS FOR STATES RELATED TO THE $^7\Sigma^+$ STATE OF FeO .

If an atomic model of $\text{Fe}^+ d^6 (sp)^1$ and $\text{O}^- p^5$ is assumed, there are a large number of ways in which the Fe $3d$ electrons can be distributed among $d\sigma$, $d\pi$, and $d\delta$ and the O $2p$ electrons among $p\sigma$ and $p\pi$. Even if we restrict ourselves to cases where the 6 d -electrons are coupled to ^5D , there are still a large number of septet, quintet, and triplet states which can be constructed. In Table III, we list all possible septet states and the $^5\Sigma^+$ states which can be constructed on this model.

We have used the $^7\Sigma^+$ SCF orbitals¹³ to construct wave functions for the $^7\Sigma^+$, $^7\Sigma^-$, $^7\Pi$, and $^5\Sigma^+$ configurations listed in Table III. For $^5\Sigma^+$, we have also constructed the nine additional configurations which arise when the Fe $3d$ electrons are not restricted to be coupled to ^5D . Clearly, no additional septet configurations can be constructed by dropping the restriction to ^5D coupling for Fe d^6 . Configuration interaction, CI

calculations were then performed using these wave functions.

The off-diagonal Hamiltonian matrix elements among the configurations listed in Table III (and, in the case of $^5\Sigma^+$, between the four configurations listed and the nine additional ones mentioned above) are negligible. The CI eigenfunctions could always be clearly identified with a single one of the configurations listed in Table III; the dominant CI coefficient for these states is always greater than 0.995. Thus the results for these states are the same as would be obtained by frozen orbital calculations. (This was not expected before the CI calculations were performed but follows for the reasons given next.) The off-diagonal matrix elements are small because of the atomic nature of the MO's and the sorts of replacements allowed between the configurations. In brief, these off-diagonal matrix elements involve only two center integrals between MO's which are essentially centered on Fe or on O. The exchange-type integrals, $[\text{FeO}|\text{FeO}]$, are small because the overlap between the Fe and O orbitals is small. The Coulomb-type integrals, $[\text{FeFe}|\text{O O}]$, are small because the angular factors involved are such that the integrals represent high order multipole interactions. There are large interactions among some of the additional $^5\Sigma^+$ configurations. However, the lowest CI eigenvector significantly involving one of these configurations is the fourth root of the $^5\Sigma^+$ CI and is ~ 2.5 eV above the lowest $^5\Sigma^+$ root; thus these states are not of particular interest.

The calculated potential curves for all the $^7\Sigma^+$, $^7\Sigma^-$, and $^7\Pi$ states and for the lowest two of the $^5\Sigma^+$ states are given in Figure 1. The CI results for the lower $^7\Sigma^+$ state (configuration 1 of Table III) are the same as the SCF results to eight significant figures. The curves for the remaining eleven $^5\Sigma^+$ states are not bound with respect to separated Hartree-Fock atoms and are above the scale of Figure 1. In Table IV, we tabulate the

calculated R_e and D_e for each of the states plotted in Figure 1. The cominant configuration in each of the states is also identified by reference to Table III. The values of R_e and D_e have been obtained by fitting a quadratic around the minimum of the curves. As usual, D_e is defined with respect to the Hartree-Fock energies of the separated atoms.

For each symmetry, the lowest state has $R_e \sim 3.7$ a.u. and $D_e \sim 1.2 - 1.5$ eV. It is quite likely that there will be states with values of R_e and D_e close to those found here for the other septet and quintet symmetries ($^7\Delta$, $^7\phi$, $^5\Sigma^-$, $^5\Pi$, $^5\Delta$, and $^5\phi$) and possibly also for some of the triplet states arising from $Fe^+[d^6(^5D)(sp)]$ and O^- .

Of course, a variational treatment of the states listed in Table IV is likely to change their energies. However, the point of these frozen orbital calculations is to show that there are several states of different symmetries but similar R_e and D_e . Because the binding is almost entirely ionic and the MO's essentially atomic orbitals, it is not likely that the frozen orbital results would be changed greatly by variational calculations.

V. ESTIMATES OF THE MOLECULAR EXTRA CORRELATION ENERGY.

The Hartree-Fock and experimental transition energies and the correlation energy changes for transitions from atomic Fe to Fe^+ and O to O^- are tabulated in Table V. The correlation energy of $Fe^+(^6D) + O^-(^2p)$ is increased by +0.38 eV with respect to the neutral atoms. If we follow the population analysis given in Table II and assume that Fe^+ in FeO is $\sim 80\%$ $Fe^+ 3d^6 4s(^6D)$ and $\sim 20\%$ $Fe^+ 3d^6 4p(^6F)$ then the correlation energy is increased by only +0.23 eV. On the model that the states of FeO considered here are basically separated ions; this means that the amount of extra molecular correlation energy is small and about .2 - .4 eV. Thus the computed

dissociation energies given in Table IV are likely to be reasonably close to the true values.

V. CONCLUSIONS

Barrow and Senior¹⁶ have suggested that the most likely ground state for FeO is a $^7\Sigma$ or $^5\Sigma$. We believe that we have investigated the possible septet configurations fairly carefully and it seems very unlikely that these dissociation energies can be significantly larger than those given in Table IV.

Brewer and Rosenblatt¹⁷ have estimated a value of $D_0^0 = 95 \pm \text{kcal/mole}$ ($4.12 \pm .22 \text{ eV}$) for FeO. A very recent thermo-chemical value of $D_0^0 = 97 \pm 3 \text{ kcal/mole}$ ($4.21 \pm .13 \text{ eV}$) has been reported by Balducci et al¹⁸. This seems to rule out a septet state and in particular a $^7\Sigma$ state as the ground state of FeO.

Several quintet states with structure quite different from the states considered here have been investigated and a large CI calculation performed on a $^5\Sigma^+$ state. For the present, we note that assuming a dissociation energy of $\sim 4.2 \text{ eV}$, then the states considered in this paper will have term energies of $\sim 2.7 \text{ eV}$. There are observed states of FeO¹⁹, the a, b, and c states with term energies of, respectively, 2.14, 2.22, and 2.79 eV. If the ground state of FeO is a quintet state, then it is possible to identify the c state with a quintet state with the structure which we have considered in this paper. The observed $^{19} \omega_e = 540 \text{ cm}^{-1}$ for the c state is in keeping with the shallow curves observed for the states reported here.

VI. ACKNOWLEDGMENTS

The author wishes to gratefully acknowledge many stimulating discussions with B. Liu, A. D. McLean, H. J. T. Preston, and M. Yoshimine.

VI. REFERENCES

1. R.S. Mulliken, J. Chem. Phys. 23, 1833 (1955).
2. C.C.J. Roethman, Rev. Mod. Phys. 32, 179 (1960).
3. C.C.J. Roethman and P.S. Bagus in Methods in Computational Physics Vol. 11. Academic Press, New York (1963).
4. C. Froese-Fischer, Computer Physics Comm. 1, 151 (1970).
5. P.S. Bagus and T.L. Gilbert (unpublished).
6. E. Clementi, Tables of Atomic Wave Functions, IBM J. Res. and Dev., 9 supplement (1965).
7. C. Froese-Fischer, "Hartree-Fock Results for the Atoms from Helium to Radon" U. British Columbia Technical Report (unpublished).
P.S. Bagus, B. Liu, and H.F. Schaeffer III, Phys. Rev. A2, 555 (1970).
Numerical HF wavefunctions for O^+ were computed using the program described in Ref. 4.
8. P.S. Bagus, B. Liu, A.D. McLean, H.J.T. Preston, and M. Yoshimine, unpublished work.
9. A.D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions", suppl. to IBM J. of Res. and Dev. 11, (1967).
10. The ALCHEMY computer programs were written by P.S. Bagus, B. Liu, A.D. McLean, and M. Yoshimine of the Theoretical Chemistry Group at IBM Research in San Jose, California. Preliminary descriptions of the program are given in A.D. McLean, "Potential Energy Surfaces from ab initio Computation: Current and Projected Capabilities of the ALCHEMY Computer Program," Proceedings of the Conference on Potential Energy Surfaces in Chemistry held at the University of California, Santa Cruz, August 1970.

11. D.R. Hartree, "The Calculation of Atomic Structures", John Wiley, New York, (1957).
C.C.J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
12. J.L. Rabin, Phys. Rev. 41, 721 (1952);
A.D. McLean, J. Chem. Phys. 40, 2774 (1964).
13. In fact, the 9σ and 10σ orbitals used for these calculations were not the canonical SCF MO's described in Section III. Small non-zero Lagrange multipliers, $\epsilon_{9\sigma, 10\sigma}$, were inadvertently introduced in the original SCF calculations used to generate the MO's for the frozen orbital work. The largest $\epsilon_{9\sigma, 10\sigma}$ is +.016 a.u. for $R = 3.4$ a.u. and the next largest is +.008 a.u. for $R = 3.6$ a.u. These non-zero Lagrange multipliers do not change any properties of the $7\Sigma^+$ wave function but they result in 9σ and 10σ orbitals which are related to the canonical orbitals by a unitary transformation. The transformation with the largest off-diagonal elements is for $R = 3.4$ and $|U_{9\sigma, 10\sigma}| = .045$, the next largest is for $R = 3.6$ and $|U_{9\sigma, 10\sigma}| = .021$. The use of the canonical 9σ and 10σ MO's would have changed some of the frozen orbital results to be described. However, because the transformations to the canonical orbitals are nearly diagonal the changes would probably not have been large. In particular, the object of the frozen orbital calculations is qualitative more than quantitative.
14. C.E. Moore, "Atomic Energy Levels" Vol. II, NBS Circular 467, U.S. Govt. Printing Office, Washington, D. C. (1952).
15. L.M. Branscomb, D.S. Burch, S.J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).
16. R.F. Barrow and M. Senior, Nature 223, 1359 (1969).

17. L. Brewer and G. M. Peschlatt, *Advan. High Temp. Chem.* 7, 46 (1969).
18. G. Balducci, G. dell'aria, M. Guido, and V. Pincante, *J. Chem. Phys.* 55, 2596 (1971).
19. *Tables of Constants and Numerical Data*, edited by S. Bourcier, Pergamon Press, Oxford (1970).

TABLE I.

The STO basis set for FeO. The molecular basis set is formed by constructing all possible σ , π , and δ basis functions from the one-center atomic STO's listed. For each one-center STO, the principle quantum number, ζ value, and exponent are listed.

Basis Functions Centered on Fe

$n\ell$	ζ	$n\ell$	ζ	$n\ell$	ζ	$n\ell$	ζ
1s	27.0596	2p	23.0394	3d	11.2792	4f	4.5
2s	23.1917	2p	13.8404	3d	5.7556	4f	2.5
3s	17.5334	2p	9.5941	3d	3.1235		
2s	10.1620	3p	5.2351	3d	1.7031		
3s	5.2935	3p	3.2100				
3s	3.5954	4p	1.8				
4s	1.9486	4p	0.9				
4s	1.0931						

Basis Functions Centered on O

$n\ell$	ζ	$n\ell$	ζ	$n\ell$	ζ
1s	13.3654	2p	7.8070	3d	4.0
1s	7.6126	2p	3.4363	3d	3.0
2s	6.2996	2p	1.7424	3d	2.0
2s	3.2045	2p	8.5650		
2s	1.7637	2p	4.7060		

Molecular Basis Set

Center	Number of functions per Symmetry		
	σ	π	δ
Fe	21	13	6
O	13	8	3
Total	34	21	9

TABLE II.

Computed SCF properties for the $7\pi^+$ state of FeO for $R = 3.2$ to 4.2 a.u. Gross atomic populations and the contributions according to λ -value are given for several orbitals. The population of an orbital is normalized to its occupation number. All values are in atomic units: 1 a.u. = 27.212 eV, 1 a.u. = 0.52916 Å and 1 a.u. = 2.342 Debye.

		R = 3.2		R = 3.4		R = 3.6		R = 3.8		R = 4.0		R = 4.2	
		Fe	O	Fe	O	Fe	O	Fe	O	Fe	O	Fe	O
7 π	Population (s)	.010	1.920	.013	1.934	.013	1.946	.012	1.957	.010	1.966	.009	1.973
	(p)	.013	.022	.013	.016	.012	.012	.010	.033	.003	.006	.007	.004
	(d)	.030	.000	.022	.000	.016	.000	.011	.000	.003	.000	.006	.000
	(f)	.004	0	.003	0	.002	0	.001	0	.001	0	.001	0
	Sum	.058	1.942	.050	1.950	.042	1.958	.034	1.966	.028	1.972	.022	1.978
<Z>		3.000	-0.200	3.230	-0.170	3.456	-0.144	3.676	-0.122	3.893	-0.102	4.114	-0.086
e		-1.2051		-1.1826		-1.1628		-1.1454		-1.1301		-1.1167	
8 σ	Population (s)	.052	.054	.069	.042	.083	.032	.065	.024	.108	.019	.119	.014
	(p)	.023	1.771	.038	1.774	.046	1.775	.049	1.776	.051	1.776	.052	1.775
	(d)	.090	.002	.072	.003	.059	.003	.050	.003	.042	.003	.035	.004
	(f)	.003	0	.003	0	.002	0	.002	0	.002	0	.001	0
	Sum	.174	1.826	.182	1.818	.190	1.810	.197	1.803	.202	1.798	.207	1.793
<Z>		3.164	-0.036	3.319	-0.081	3.466	-0.132	3.616	-0.184	3.765	-0.235	3.916	-0.284
e		-0.5526		-0.5101		-0.4839		-0.4639		-0.4500		-0.4324	
9 σ	Population (s)	.039	.004	.027	.003	.019	.002	.014	.001	.010	.001	.008	.001
	(p)	.017	.034	.013	.024	.011	.018	.003	.014	.006	.011	.003	.008
	(d)	.935	.000	.932	.000	.953	.000	.963	.000	.972	.000	.978	.000
	(f)	.000	0	.000	0	.000	0	.000	0	.000	0	.000	0
	Sum	.962	.038	.973	.027	.980	.020	.985	.015	.989	.011	.991	.009
<Z>		0.051	-3.139	0.032	-3.368	0.014	-3.586	0.003	-3.797	-0.004	-4.004	-0.003	-4.208
e		-0.6235		-0.6472		-0.6669		-0.6837		-0.6985		-0.7115	

	R = 3.2			R = 3.4			R = 3.6			R = 3.8			R = 4.0			R = 4.2		
	Fe	O		Fe	O		Fe	O		Fe	O		Fe	O		Fe	O	
10+ Population (s)	.777	.000		.768	.000		.766	.000		.803	.000		.808	.000		.813	.000	
(p)	.238	-.024		.224	-.018		.211	-.011		.199	-.005		.188	.002		.177	.001	
(d)	.009	.000		.006	.000		.004	.000		.003	.000		.002	.000		.002	.000	
(f)	.000	0		.000	0		.000	0		.000	0		.000	0		.000	0	
Sum	1.024	-.024		1.018	-.018		1.011	-.011		1.005	-.005		.999	.001		.992	.001	
<z>	-1.565	-4.765		-1.500	-4.000		-1.437	-5.037		-1.373	-5.173		-1.306	-5.306		-1.236	-5.436	
σ	-0.2632			-0.2903			-0.2970			-0.3035			-0.3098			-0.3160		
3+ Population (p)	.008	-.010		.006	-.008		.004	-.006		.003	-.004		.002	-.002		.002	-.002	
(d)	3.002	.000		3.002	.000		3.002	.000		3.002	.000		3.001	.001		3.001	.001	
(f)	.000	0		.000	0		.000	0		.000	0		.000	0		.000	0	
Sum	3.010	-.010		3.008	-.008		3.006	-.006		3.005	-.005		3.004	-.004		3.003	-.003	
<z>	-0.042	-3.242		-0.037	-3.437		-0.032	-3.632		-.028	-3.828		-0.025	-4.025		-0.023	-4.223	
σ	-0.6076			-0.6148			-0.6228			-0.6313			-0.6399			-0.6484		
4+ Population (p)	.066	2.915		.055	2.928		.046	2.940		.033	2.949		.032	2.958		.027	2.965	
(d)	.005	.005		.005	.005		.005	.005		.005	.005		.004	.003		.004	.003	
(f)	.008	0		.006	0		.004	0		.003	0		.002	0		.002	0	
Sum	.079	2.921		.066	2.934		.055	2.944		.046	2.954		.039	2.961		.032	2.968	
<z>	3.698	-0.102		3.305	-.095		3.512	-0.093		3.713	-0.091		3.926	-0.074		4.134	-0.066	
σ	-0.5117			-0.4938			-0.4765			-0.4632			-0.4534			-0.4428		
16 Population (d)	2.000	.000		2.000	.000		2.000	.000		2.000	.000		2.000	.000		2.000	.000	
(f)	.000	0		.000	0		.000	0		.000	0		.000	0		.000	0	
Sum	2.000	.000		2.000	.000		2.000	.000		2.000	.000		2.000	.000		2.000	.000	
<z>	-0.001	-3.201		-0.002	-3.402		-0.002	-3.602		-0.002	-3.802		-0.002	-4.002		-0.002	-4.202	
σ	-0.7134			-0.7214			-0.7300			-0.7385			-0.7472			-0.7555		
Total Population	25.294	8.706		25.290	8.710		25.281	8.719		25.270	8.730		25.258	8.742		25.247	8.753	
E	-1337.26304			-1337.28704			-1337.29670			-1337.29745			-1337.29280			-1337.28499		
V/T	-1.9995988			-1.9999018			-1.9999405			-2.0000350			-2.0000957			-2.0001382		
u	-0.786			-1.016			-1.244			-1.472			-1.701			-1.931		

TABLE III.

Configurations for Septet States and for $5\pi^+$ states which can be constructed for FeO from an atomic model of $Fe3d^6(3s)(4s)^1$ and $O2s^2(2p)$. The number of electrons in each shell is given and for each π and δ shells, the coupling of the shell is given in parenthesis. The Fe d electrons are coupled to each other and then to the 4s electron. The O π electrons are coupled to each other. The notation 4sp indicates that the Fe δ orbital is a hybrid (c.f. the 10s orbital in Table II).

Orbital Occupation and Coupling									
Total Symmetry	3d δ	3d π	3d δ	Fe d-shell coupling	4s π	Fe coupling 2oc	2 π^+	0 coupling	
1. $7\pi^+$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	6π	$3(2\pi)$	2π	
2. $7\pi^+$	2	$2(3\pi^-)$	$2(3\pi^-)$	$5\pi^+$	1	$6\pi^+$	4	$2\pi^+$	
3. $7\pi^-$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi)$	$2\pi^-$	
4. $7\pi^-$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	6π	4	$2\pi^+$	
5. $7\pi^-$	1	$2(3\pi^-)$	$3(2\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi^-)$	$2\pi^-$	
6. $7\pi^-$	2	$2(3\pi^-)$	$2(3\pi^-)$	$5\pi^+$	1	$6\pi^+$	$3(2\pi)$	2π	
7. $7\pi^-$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi)$	$2\pi^-$	
8. $7\pi^-$	1	$2(3\pi^-)$	$3(2\pi^-)$	$5\pi^-$	1	$6\pi^-$	4	$2\pi^+$	
9. $7\pi^-$	1	$2(3\pi^-)$	$3(2\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi)$	2π	
10. $5\pi^+$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi)$	$2\pi^-$	
11. $5\pi^+$	1	$3(2\pi^-)$	$2(3\pi^-)$	$5\pi^-$	1	$6\pi^-$	$3(2\pi)$	$2\pi^-$	
12. $5\pi^+$	2	$2(3\pi^-)$	$2(3\pi^-)$	$5\pi^+$	1	$6\pi^+$	4	$2\pi^+$	
13. $5\pi^+$	2	$2(3\pi^-)$	$2(3\pi^-)$	$5\pi^+$	1	$6\pi^+$	4	$2\pi^+$	

TABLE IV.

Values of R_e and D_e for Frozen Orbital Calculations on FeO. The dominant configuration for each state is identified by reference to the list given in Table III.

Symmetry	Dominant Configuration	R_e (a.u.)	D_e (eV)
7_{Σ}^{+*}	1	3.73	1.24
7_{Σ}^{+}	2	3.90	-0.60
7_{Σ}^{-}	3	3.74	1.21
7_{Π}	5	3.69	1.46
7_{Π}	6	3.83	0.79
7_{Π}	4	3.72	0.06
5_{Σ}^{+}	10	3.74	1.15
5_{Σ}^{+}	11	3.71	0.20

*These results are identical to the SCF results for this state to eight significant figures.

TABLE V.

Calculated and Experimental Transition
Energies and Correlation Energy Changes
in Fe and O. Energies are in eV.

State	Calculated ^a HF Energies	Experimental Energies	ΔE Correlation
Fe $3d^6(5D)4s^2$	0	0	-----
Fe ⁺ $3d^6(5D)4s; 6D$	6.275	7.898 ^b	-1.623
Fe ⁺ $3d^6(5D)4p; 6F$	10.751	13.101 ^b	-2.350
O $2p^4(3p)$	0	0	
O ⁻ $2p^5(2p)$	+0.541	-1.456 ^c	+2.006

a. The HF energies are obtained from numerical Hartree-Fock calculations using a program of C. Froese-Fischer. See Ref. 7.

b. See Ref. 14.

c. See Ref. 15.

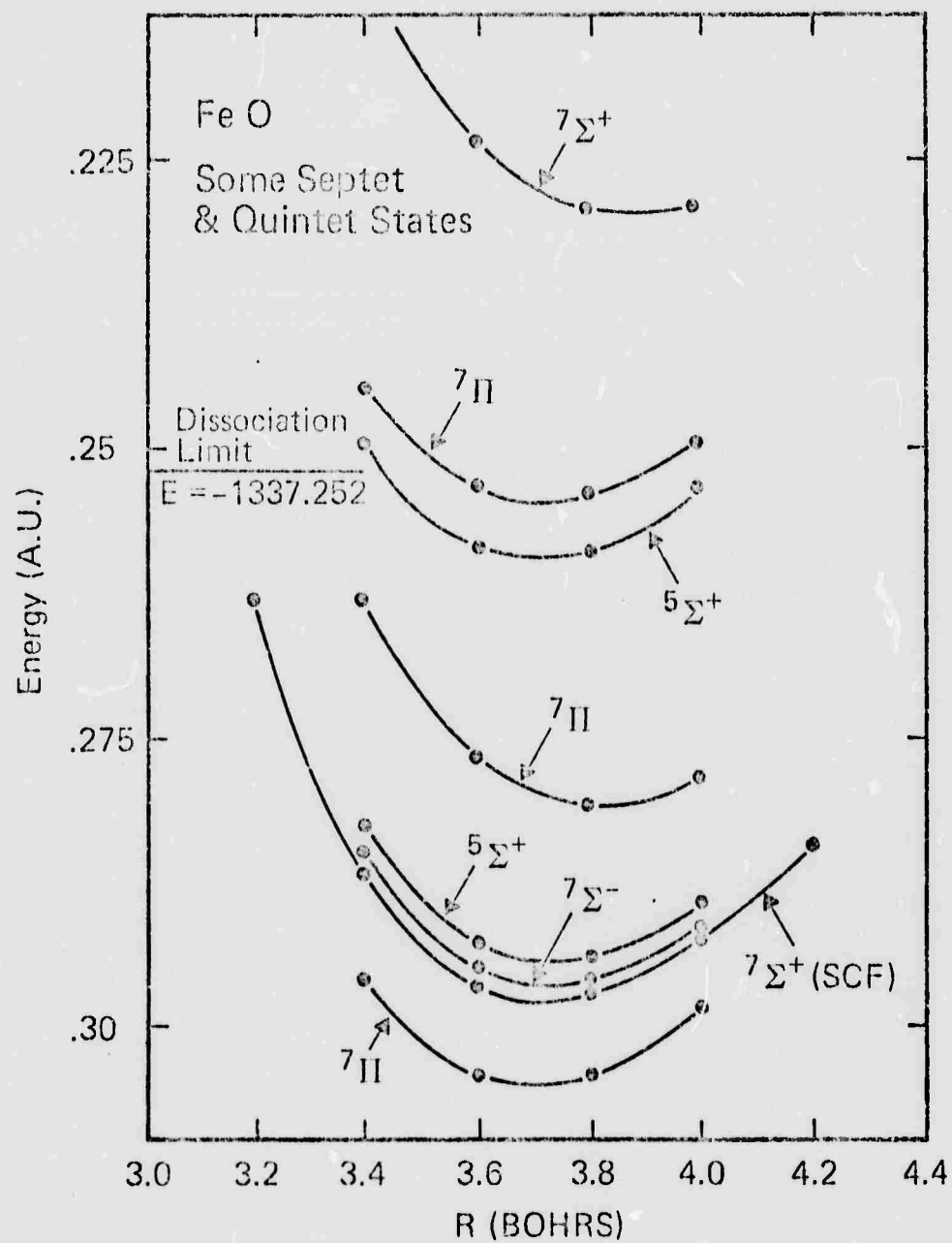


Figure 1. Potential curves for several Septet and Quintet States of FeO. The lower $7\Sigma^+$ curve is obtained from SCF calculations; the remaining curves are obtained from frozen orbital calculations using the $7\Sigma^+$ SCF MO's as described in Sec. III. The dissociation limit is for the SCF energies of the ground state Fe and O atoms.